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ALUMINUM SPECIATION IN WATERS OF NOVA SCOTIA AND THEIR IMPACT ON WATER QUALITY BRANCH ANALYTICAL AND FIELD METHODS

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ABSTRACT

High levels of ionic or labile aluminum in acid freshwaters have been linked to the mortality of fish and other aquatic biota. A major problem in assessing the potential toxicity of Al in waters however, is that few laboratory analytical methods address the problem of measuring the labile fraction as opposed to some measure of "total" aluminum. This study was designed to assess the use of a speciation method, the Chelex-100 method (Campbell et al. 1984) under field conditions, to measure the labile Al levels in representative waters of Nova Scotia and to make recommendations on future directions in speciation work in the region.

The major findings of this study were that in the organic acid rich waters of Nova Scotia, extractable Al concentrations correlated very well with dissolved organic carbon levels, and that there seems to be little labile Al in brown waters. Because of these findings, no changes in field and analytical procedures are recommended for the regular monitoring programs. Despite this conclusion, however, we should continue speciation studied under special environmental conditions such as snow melts. Also, other speciation methods should be used to confirm these preliminary results.

RESUME

Des concentrations elevees d'aluminium ionique dans les eaux douces acides sont probablement responsables pour la mortalite de poissons et d'autres animaux aquatiques. Un des problemes que l'on retrouve en essayant d'analyzer le potentiel toxicologique de ces eaux, est qu'il est tres difficile de determiner la fraction ionique de l'aluminium "totale".

Le but de cette etude etait d'utiliser une methode developpe par Campbell et al. (1984), la methode Chelex-100, pour determiner son utilite dans des conditions operationelles, pour mesure les concentrations d'aluminium ionique dans les eaux de la Nouvelle-Ecosse, et pour voir si l'on devait changer nos methodes d'echantillonage ou d'analyse.

Nos resultats ont demontre que dans des eaux riches en substances organiques, comme l'on trouve en Nouvelle-Ecosse, une bonne correlation fut etablie entre l'aluminium extractible et le carbone organique dessout. Aussi, peu d'aluminium ionique fut mesure dans les eaux brunes. En tenant compte de ces resultats, aucuns changements de nos procedures habituelles sont recommandes au terrain ou au laboratoire pour nos programmes de monitorage. Malgre cette conclusion, il faut toutefois continuer nos etudes de speciation sous d'autres conditions environnementales, comme durant des fontes de neige. Aussi, il est toujours necessaire d'utiliser d'autres methodes de speciation pour confirmer ces résultats préliminaires.

INTRODUCTION

Increases in acid precipitation in non-calcareous watersheds have been correlated with the accelerated leaching of aluminum from soils and sediments (Cronan and Schofield 1979). Driscoll et al. (1980) have shown that only the inorganic (labile) fraction of aqueous aluminum is toxic to adult fish, while Baker and Schofield (1982) have extended this work to show that labile Al affects various fish life stages.

The waters of Atlantic Canada, particularly of southwestern Nova Scotia, present a number of challenges which make an estimate of the labile Al concentrations very important. Watt et al. (1983) report the decrease of Atlantic salmon (Salmo salar) populations in a number of rivers in Nova Scotia, a decrease which they attribute to acidification effects, though no cause-effect relationship was shown. Lacroix et al. (1983) also show that salmon fry, exposed to Westfield River (Nova Scotia) water at its mean summer pH of 5.0 die within 25 days, unlike controls at pH 6.0. These studies show that populations are reduced by acidification, though the actual mechanism for causing fish mortality has not yet been fully elucidated. One of the possible causes for these fish mortalities is aluminum toxicity.

The chemistry of aluminum in natural waters is very complex. Analytical and sampling methods used in the past by Environment Canada and other agencies have not taken into consideration the speciation of

Al, a factor of importance in assessing its toxicity. Aluminum can form strong complexes with fluoride, sulphate and dissolved organic ligands (Driscoll et al. 1980), the last two of which are common in Atlantic Canadian waters. Driscoll et al. (1980) have also shown that organically bound aluminum is not toxic to fish, and have shown that in waters high in dissolved organic carbon (DOC), non-labile aluminum forms the predominant fraction of total aluminum.

When we tried to apply these observations to Atlantic provinces waters two questions arose. Firstly, what are the differences in organic ligand composition between their waters and ours? Secondly, what about the demonstrated analytical interferences (Playle et al., 1982) with the ferron method used by Driscoll et al., 1980? The answers to these questions could significantly affect any relationship between DOC and Al.

Up until the time of this study, two methods were routinely used by the Water Quality Branch for aluminum analysis. The one which has been in use longest, is chelation by oxine at pH 8.3, extraction of the complex into $CHCl_3$ or MIBK, with subsequent determination by atomic absorption. The second, which has not been used extensively, is atomic absorption spectrometry using a graphite furnace. Results of both these methods have usually been considered to give an estimate of total Al, an assumption shared by Playle et al. (1982) in the case of atomic absorption spectrometry with graphite furnace.

digestion?

Samples collected in the field by WQB for analysis by either method are preserved by adjusting the samples to pH 2 with concentrated nitric acid, a procedure which is obviously inappropriate for determination of Al species. WQB-AR does not routinely filter its water samples as filterable residues are commonly less than two $mg.L^{-1}$. It can be assumed that the filterable material is associated with clays, silts and other particles and so is not biologically available, however quantification of its magnitude has not been done routinely in this region.

There have been other methods proposed for measuring the levels of labile Al found in natural waters. LaZerte (1984) has proposed a 15 second oxine reaction at pH 8.3, a method similar to present WQB techniques, and which has the same limitations. Campbell et al. (1983) have used a chelating resin approach on water at in-situ pH levels. This method seems more appealing, as it does not change the speciation state of the aqueous aluminum, and because its mechanism of action more closely resembles the toxicity mechanisms that operate on biota. As the Campbell et al. (1984) method, which will be called the Chelex-100 method in this report, seemed to provide information on the state of Al speciation and as it seemed to be the most useful of the speciation methods being used, we decided to use it on Nova Scotia waters with three goals in mind. Firstly, we wanted to measure operationally defined (by the method) labile Al levels in Nova Scotia waters. Secondly, we wanted to compare the Chelex-100 procedure to other methods presently in use by WQB-AR, and thirdly, make recommendations as to future uses of Al speciation methods by WQB-AR.

AREA AND METHODS

Four sampling runs were done in 1983 to gather data on the seasonal variability of labile aluminum levels and effects of treatment. Five sites were sampled in March. After studying the results, it was decided that a greater range of DOC values among the sites would be advantageous, so two more sites were added for the May trip. As the two additional stations provided the DOC range needed, two of the March sites were then dropped.

Table 1 gives the names and sizes of the basins sampled. Grafton, Roger's and Beaverskin Brooks are in Kejimkujik National Park, as is the Mersey River sampling site. Whitburn and Moose Pit Brooks are part of the Medway River system, a few kilometers east of the Park. Little Springfield lake was chosen due to the extreme pH conditions we knew existed. It is located on an exposed slate bed with high pyrite content in Lower Sackville, a suburb of Halifax, and was included as a control on the chelation method.

Sample treatments evolved from one sampling trip to the next, as methods were modified to take the previous trip's results into consideration. At each sampling, a one litre sample was taken for major ion and DOC analyses. Some samples from the May sampling were accidentally contaminated, so values from sampling dates close to the Al sampling are reported instead.

TABLE 1. BASINS SAMPLED, THEIR SIZE AND FREQUENCY OF SAMPLING FOR THIS STUDY

	Times Sampled				Basin size
	March	May	August	September	(km^2)
Grafton	X	X			52.9
Whitburn	X	X			7.1
Roger's	X	X	X	X	10.0
Mersey	X	X	X	X	297.
Moose Pit	X	X	X	X	16.7
Beaverskin		X	X	X	1.9
L. Springfield		X	X	X	0.5

At each site, a 500 mL water sample was taken and preserved immediately with 1 mL analytical grade concentrated nitric acid, the standard Water Quality field method where no filtering was done. A one litre sample was also taken, filtered in the field within a few hours of collection and subdivided for various treatments. On all sampling trips, an aliquot was filtered and preserved with concentrated nitric acid. The remainder of the sample was subdivided and treated according to procedures described below. Deionized water blanks were filtered and acidified fo quality control on all trips and showed no contamination. Figure 1 shows the flow of the procedures.

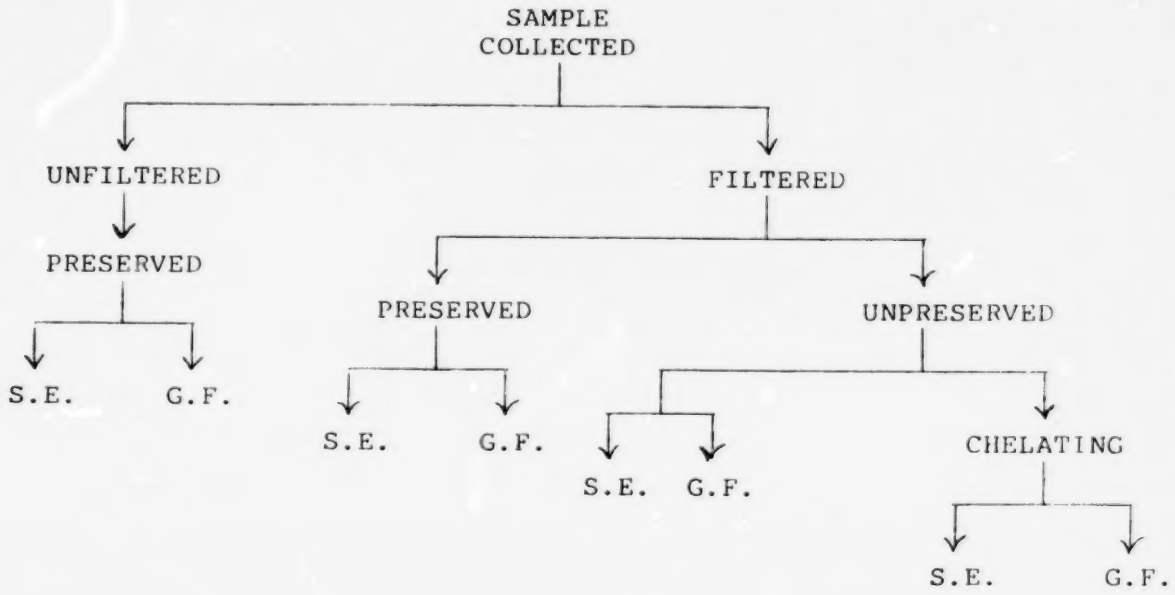
The samples were transported from the field to the laboratory at ambient temperature, were usually analyzed within 48 hours of sampling, and never later than 96 hours. All samples were analyzed using the two WQB-AR methods, the solvent extraction (oxine) (S.E.) atomic absorption method used routinely by the Water Quality Branch - Atlantic Region (detection limit 10 $ug.L^{-1}$) and the graphite furnace (G.F.) atomic absorption method (D.L. = 5 $ug.L^{-1}$) (WQB 1979).

Samples for the March and May runs, when methods were being worked out, were analyzed only once. These single values are reported. Samples for the August and November efforts were all analyzed in triplicate. Little variability was noted within samples and so only mean values are reported and used in the data analysis.

The Campbell et al. (1983) method was designed to not only

FIG. 1 - Flow diagram of analytical procedures used in the study

S.E. and G.F. refer to solvent extraction and graphite furnace methods respectively.

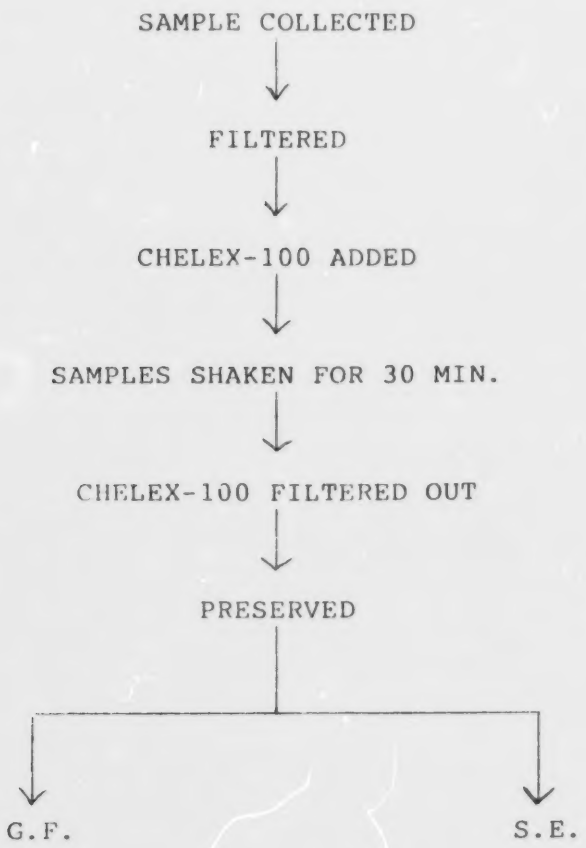


determine the labile fraction of total aluminum, but also where the other fractions were tied up. As we were only interested in the labile fraction of total aluminum, we did not try to directly determine the fraction bound to the material filterable by the 0.4 um filter, nor did we attempt to photooxidize the organic matter in the water to release the fraction bound to it. We did however, follow the remaining analytical steps which gave the labile aluminum fraction. Figure 2 shows the analytical steps taken in the study.

The chelation, using Chelex-100 resin, as proposed by Campbell et al. (1983) was done in the laboratory with the March samples. In August and November, the resin was added, the sample shaken and resin filtered out in the field after field filtering of the water. The emphasis on the May trip was to study potential Al loss to the bottle walls, so no chelation was done.

FIG. 2 - Procedures used in this study for chelation of samples (modified Campbell *et al*. 1984 method)

S.E. and G.F. refer to solvent extraction and graphite furnace methods respectively



RESULTS

Characterization of Basin Waters

Table 2 shows the major chemical parameters of interest in the undisturbed study sites. These are in wooded basins and show typical regional values of pH, dissolved organic carbon (DOC), colour and solvent extraction aluminum. At all these sites, waters were dilute with alkalinity levels below 10 $mg.L^{-1}$. DOC showed a wide range of values, with the lowest being in March and May. Values then tended to rise for the remainder of the year. pH values were generally low, as are those from most basins in southwest Nova Scotia. When all sites were taken as a group, no seasonal trends in pH could be discerned over the study period. Extractable Al (unfiltered) trends were difficult to establish over the study, but Moose Pit Brook did tend to increase over the study period. This did not seem to occur at the other sites.

Parameter values measured for the Little Springfield basin showed atypical water chemistry. Water pH was near 3.5 during all three visits. Sulfate was 54 $mg.L^{-1}$ and the other major ion parameters seemed to reflect road salting effects. DOC levels were low, between 0.6 and 2.0 $mg.L^{-1}$. Probably because of the high acidity, S.E. Al levels ranged from 2700 to 3300 $ug.L^{-1}$, values over one order of magnitude greater than those from the other sites.

TABLE 2. VALUES FOR MAJOR IONS AND OTHER PARAMETERS AT THE UNDISTURBED SAMPLING SITES

Site	pH	sp. cond. uS.cm^{-1}	Tur. JTU	Alk. mg.L^{-1}	SO4 mg.L^{-1}	DOC mg.L^{-1}	Ext. Al ug.L^{-1}
			March 10, 1983				
Grafton Bk.	5.7	36	0.7	1.0	2.5	5.4	84
Whitburn Bk.	5.2	45	0.5	0.3	3.2	4.6	60
Roger's Bk.	5.1	33	0.7	0.1	3.6	4.9	86
Mersey River	4.9	35	1.0	-0.3	3.5	9.0	175
Moose Pit Bk.	4.6	32	0.6	-0.9	2.9	9.0	155
			May 26, 1983				
Grafton Bk.	5.5	29	1.2	0.6	2.0	4.5	123
Whitburn Bk.	6.0	29	0.7	2.2	-	4.2	147
Roger's Bk.	5.2	29	1.4	0.6	2.6	7.7	217
Mersey River	4.9	29	1.0	-0.2	2.4	7.6	217
Moose Pit Bk.	4.6	33	0.4	-0.8	-	9.0	277
Beaverskin Bk.	5.4	22	0.6	0.1	2.0	1.9	90
			August 2, 1983				
Roger's Bk.	5.6	32	2.2	2.2	2.3	12.0	120
Mersey River	5.3	30	0.9	0.4	2.5	9.4	170
Moose Pit Bk.	4.7	36	0.6	-0.8	1.8	26.0	320
Beaverskin Bk.	5.6	23	0.6	0.1	1.9	2.2	< 50
			October 25, 1983				
Roger's Bk.	4.8	53	1.4	0.3	5.3	16.0	260
Mersey River	5.7	33	1.0	2.2	3.1	10.0	180
Moose Pit Bk.	4.6	45	0.6	-0.9	2.3	31.0	400
Beaverskin Bk.	5.6	23	0.7	-0.2	2.3	2.2	30

Aluminum Analytical Results

The two methods of analysis for aluminum were used on the acidified filtered samples: atomic absorption using solvent extraction and atomic absorption using graphite furnace. Comparison of these techniques (Table 3) using a non-parametric sign test indicated that the null hypothesis of no difference between the two treatments, was rejected and that graphite furnace values were significantly higher at the 99% level than for solvent extraction by a mean of 10%, a median of 3 percent, and a range of between 34 and -27 percent. Despite this result on overall data, there seemed to be little difference in the results from the two methods for Roger's and Beaverskin Brooks and Mersey River. Both Roger's and Mersey sites had higher turbidity levels than the other watercourses, though this should not be a factor as the Al samples were initially filtered. Beaverskin Brook values were very low, and the differences between the two methods might simply be an artifact of analytical precision at these levels.

Despite the lower values measured using S.E., the results measured using this analytical technique will be reported in the remainder of this report for two reasons. The first is that it is commonly used by most laboratories, and so is best for intercomparisons with other work. The second is that the Al fraction not extracted by the oxine method, but measured as total by G.F. is not likely to be available to biota. As a strong chelator cannot extract this fraction, it is not likely to be of interest to toxicologists.

Total or total filtered

TABLE 3. COMPARISON OF Al LEVELS MEASURED ON FILTERED, ACIDIFIED SAMPLES USING SOLVENT EXTRACTION (S.E.) AND GRAPHITE FURNACE (G.F.) METHODS. ALL VALUES IN $ug.L^{-1}$

	March		May		August		October	
	S.E.	G.F.	S.E.	G.F.	S.E.	G.F.	S.E.	G.F.
Grafton Bk.	74	90	80	108	-	-	-	-
Whitburn Bk.	64	90	90	120	-	-	-	-
Roger's Bk.	88	90	165	166	-	-	280	287
Mersey R.	184	190	220	178	170	160	145	145
Moose Pit Bk.	138	210	230	283	300	350	280	410
Beaverskin Bk.	-	-	60	78	50	20	30	22

Effect of Sample Filtration

Filtered, acidified samples were compared to non-filtered, acidified ones, for all four sampling runs. Values reported here are from S.E. only, though G. F. analyses gave the same results. Using a Wilcoxon one-tailed test for paired observations on data from each sampling, it was found that the non-filtered aluminum levels were significantly higher at the 99% level from the filtered samples by an average of 9.8 percent, with values ranging from -7 percent to +39 percent (Table 4). The May and October samplings showed the largest differences between the treatments, though no correlation could be established between filterable Al and any of the parameters measured by this study, including turbidity. In Little Springfield Lake, filtration caused no reduction in Al levels.

Effect of Sample Acidification

The Campbell et al. (1983) method, as originally developed, involved bringing unpreserved samples from the field to the laboratory, under cool conditions. A comparison was then made between samples filtered and preserved in the field, and those filtered and not preserved to determine if a loss of aluminum occured under unacidified conditions. Of the 15 samples in undisturbed basins where comparisons could be made (Table 5), all showed acidified samples with higher values

TABLE 4. PERCENT LOSS or (GAIN) of SOLVENT EXTRACTABLE Al AFTER FIELD FILTRATION

Site	Sampling Data March %	May %	August %	October %
Grafton Bk.	12	9	-	-
Whitburn Bk.	(7)	39	-	-
Roger's Bk.	(2)	24	0	(6)
Mersey River	(5)	(1)	0	17
Moose Pit Brook	11	17	6	30
Beaverskin Brook	-	33	0	0

TABLE 5. COMPARISON OF ALUMINUM LEVELS IN FILTERED ACIDIFIED (ACID) AND UNACIDIFIED (NO) SAMPLES. (VALUES IN $ug.L^{-1}$)
AUGUST SAMPLES WERE NOT ANALYZED BY S.E.

	March		May		October	
	ACID	NO	ACID	NO	ACID	NO
Grafton Brook	74	50	80	53	-	-
Whitburn Brook	64	30	90	50	-	-
Roger's Brook	88	60	165	125	280	232
Mersey River	184	95	220	135	137	120
Moose Pit Brook	138	90	230	220	283	268
Beaverskin Brook	-	-	60	50	30	12

than unacidified. Median loss was 33 percent with a range of 4 to 60%. This result shows that returning samples from the field to the laboratory involves the loss of an important fraction of non-filterable aluminum. Sample acidification in the Little Springfield Lake samples showed somewhat ambiguous effects, as acidified values in May, August and October were 3800, 2700 and 3400 ug.L^{-1} while untreated samples gave 3400, 2800 and 3300 ug.L^{-1}. These are most likely a result of the precision of the method and the accuracy of the sampling technique. In proportional terms, the discrepancies are very small, though in absolute terms, they are more impressive.

Use of Chelating Resins

Chelation of the samples using the Chelex-100 method in the laboratory was done on samples collected during three field trips. Results from March (Table 6) indicated that no labile fraction was removed from water. We considered that this fraction might be lost to the walls during transportation and storage before the chelating agent was added so we therefore tried another tactic. This involved chelating the samples in the field, within a few hours of sampling. Once treated, the samples were acidified for transportation to the laboratory. Table 6 shows the results of this approach which was used in the August and October samplings. In the Table the " acidified only " samples give an indication of " Total " non-filterable aluminum while the "Chelex" samples show the Al left after chelation of the labile fraction had occured. In both laboratory and field chelation of Little Springfield

TABLE 6. COMPARISON OF NON-FILTERABLE Al FROM FILTERED, ACIDIFIED SAMPLES WITH THOSE TREATED WITH CHELEX-100 RESIN IN THE LABORATORY AND IN THE FIELD, THEN ACIDIFIED (VALUES IN $ug.L^{-1}$)

	March (in lab)		August (in field)		October (in field)	
	acidified only	chelex	acidified only	chelex	acidified only	chelex
Grafton Bk.	50	53	-	-	-	-
Whitburn Bk.	35	51	-	-	-	-
Roger's Bk.	60	58	100	140	275	280
Mersey River	115	121	170	110	150	120
Moose Pit Bk.	95	128	270	300	280	410
Beaverskin	-	-	20	25	40	38

samples, Al values were reduced from over 3000 $ug.L^{-1}$ to below 50 $ug.L^{-1}$. These results seem to show an increase in total Al after chelation. As the Chelex-100 resin was tested for contamination and found to not increase Al levels of blanks, this seems unlikely, so the increases must be due to analytical precision.

Discussion

The major ion chemistry and other parameters show the undisturbed study basins to be representative of others found in the area (Kerekes et al. 1983). The most notable features are the dilute nature of the surface waters, low pH's and the frequency of highly organic waters. These typify much of Atlantic Canada waters and provide the difficulty in the interpretation of aluminum speciation work.

The comparison between graphite furnace (G.F.) and solvent extraction (S.E.) methods on natural filtered samples provides the first interpretation challenge. Sample digestion by nitric acid will make available for extraction all Al released at pH 1.5-2.0. The Al not released will most likely be associated with the sample's suspended solid or colloid component. The lower the suspended solids, the more S.E. values should approximate "total Al". The G.F. results are probably the more closely related to total Al of the two and have been used as such in other studies (Playle et al. 1982).

A factor which was seen to correlate with Al concentration was DOC, a parameter which gives an indication of the levels of large and small molecular weight organic acids and other decomposition and metabolic by-products which are found in natural waters. A linear correlation between DOC and unfiltered S.E. Al using all undisturbed basins showed the following relationship, which is similar to what has also been reported by Driscoll (1984).

S.E. Al = 11.5 {DOC} + 43, r^2 = 0.86, n=19.

where Al is in $ug.L^{-1}$ and DOC in $mg.L^{-1}$

If filtered S.E. Al values are used, the relationship is also similar:

S.E. Al = 9.5 {DOC} + 59, r^2 = 0.84, n=19.

The results of the Chelex-100 work shed some light on the affinity which DOC and Al have for each other. Table 6 shows that the chelation, done either in the laboratory or in the field did not reduce Al levels from samples taken in the undisturbed basins. As chelation of the Little Springfield samples removed most Al, and so showed that the method worked, it must be that the aluminum in undisturbed basins was probably already chelated to the organic molecules in the water. The DOC concentration in water, and thus Al, are functions of basin characteristics which are not amenable to easy analysis. Basin size within the group studied did not correlate with DOC, Al or pH. The factors most likely to affect DOC are the presence or absence of bogs and marshes, soil composition, groundwater inputs and land use, none of which were studied in this exercise.

Baker and Schofield (1982) have shown that labile Al can have deleterious effects on fish at concentrations near 50 $ug.L^{-1}$ The results from this study (Table 6) show no loss of Al to the chelating

material in the natural, undisturbed basins except for the Mersey River in August where 60 ug.L^{-1} labile Al were measured. However, because of the probable analytical precision with the other samples or natural variability of samples, this value is somewhat suspect. The replicate analyses were usually within a ±10% range of each other and outliers, when they occurred were always rejected and retested. No work was done on the replication of sampling which may have shed some light on this discrepancy.

Initially, the loss of Al when samples were unpreserved cast some doubt on the accuracy of stating that no labile Al was in the sample, as it was originally felt that the fraction lost was labile. Kramer (pers. comm.) has suggested that the Al loss during transport and storage was due to polynucleic molecules, (ie non-labile) adsorbing onto the walls. Evidence from the Little Springfield samples confirm this hypothesis. DOC levels there were low at 1.1, 0.6 and 2.0 mg.L^{-1} in May, August and October. Preserved Al levels at those sampling times were 3800, 2700 and 3400 ug.L^{-1}. Unacidified sample values were 3400, 2800 and 3300 ug.L^{-1} Al. Though Al values here were very high compared to the undisturbed sites, little loss of Al on a percent basis was measured. This result also agrees with Campbell et al (1982) where their standard solutions showed no loss of Al in storage.

This work showed that the Chelex-100 method worked in Little Springfield Lake, where conditions were ideal for its use. As all sampling and analytical methods were identical at the other sites in

August and October, it must be assumed that the answers we have are valid and reflect natural conditions. Based on the above data, it can then be argued that in natural, podzolic basins with thin soil layers in Atlantic Canada, most of the aluminum measured by S.E. is not labile. As these types of overburden conditions are found in most of Nova Scotia, all of Newfoundland and Labrador and in parts of southern New Brunswick, other causes may have to be found to explain the results shown by Watt et al 1983. However, a phenomenon has been reported elsewhere and in Nova Scotia, which suggests that some caution should be used in dealing with aluminum. Clair (M.S.) has measured pH depressions at the Mersey River site to values below 4.0 during snowmelts and rainfalls. Theoretical considerations which have been elaborated by Kramer (1983) and Driscoll (1984) suggest that under acid shock conditions, some Al may be dissociated from the organics and sediments and be in the water in labile form. Driscoll (1984) has studied this problem in laboratory setting and has shown an increase of 25% of labile Al in organic waters at pH 3.3. A measure of S.E. Al using standard WQB methods would not measure this shift in composition, so that the chelation method is the only one which would give us the information we need. Despite the prevalence of waters high in DOC in the region, there are also a number of acid rivers which may still have high labile Al levels. Unlike Beaverskin Lake which is a headwater lake, these rivers have large watersheds and probably receive Al inputs from groundwaters. These should be studied to ensure that the conclusions arrived at in this report can be extrapolated to cover the whole of Nova Scotia.

The use of the Campbell et al. (1984) method in this study has shown a number of problems which seem to limit its usefulness in large scale field studies. Despite some evidence that there is little labile Al loss during storage and transport, there is no clear assurance yet that this is the case. In order to feel more confident of the data, we recommend that the chelation step should be done as soon as possible after collection in the field. Once chelated, samples can be preserved for longer shelf life.

As Al levels from many Atlantic Canadian watersheds probably are controlled by the same phenomena as the natural ones studied, a number of assumptions can be made concerning the aluminum data already collected in the region. The Chelex-100 method has suggested that little labile Al is present in our waters. This in itself is an important fact, and further refinements in our knowledge vis a vis acid shocks and basins with different characteristics can now be studied more closely. The S.E. results which we have collected in the past are difficult, if not impossible to interpret in terms of toxicological effects, but may be of great use in assessing long-term trends in basin acidification. A current hypothesis of soil acidification effects (Cronan and Schofield 1979) is that Al is mobilized by increases in soil levels of hydrogen ions. We have been measuring Al using the S.E. approach on unfiltered samples, for over 10 years, and this study suggests that the method may still be acceptable for trend assessment purposes. Though we have arrived at fairly conclusive results in describing aluminum speciation in some of our waters, it would be of great use to us, if we were able

to confirm our findings using another method. To this end, WQB will be monitoring other speciation methods and will consider trying some of them out, should the need for more data ever arise. WQB should then continue using S.E. on unfiltered samples in all its monitoring operations. It should only use the Chelex-100 method in special studies which emphasize understanding the potential Al toxicity of regional waters. Using both or either approach when necessary, we can thus better understand the role that aluminum and its labile species play in our waters.

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